SCR Catalyst Performance on U.S. Coal Fired Boilers

2002 Conference on Selective Catalytic Reduction and
Non-Catalytic Reduction for NOx Control

Pittsburgh, Pennsylvania, USA

May 16, 2002

Presented

By

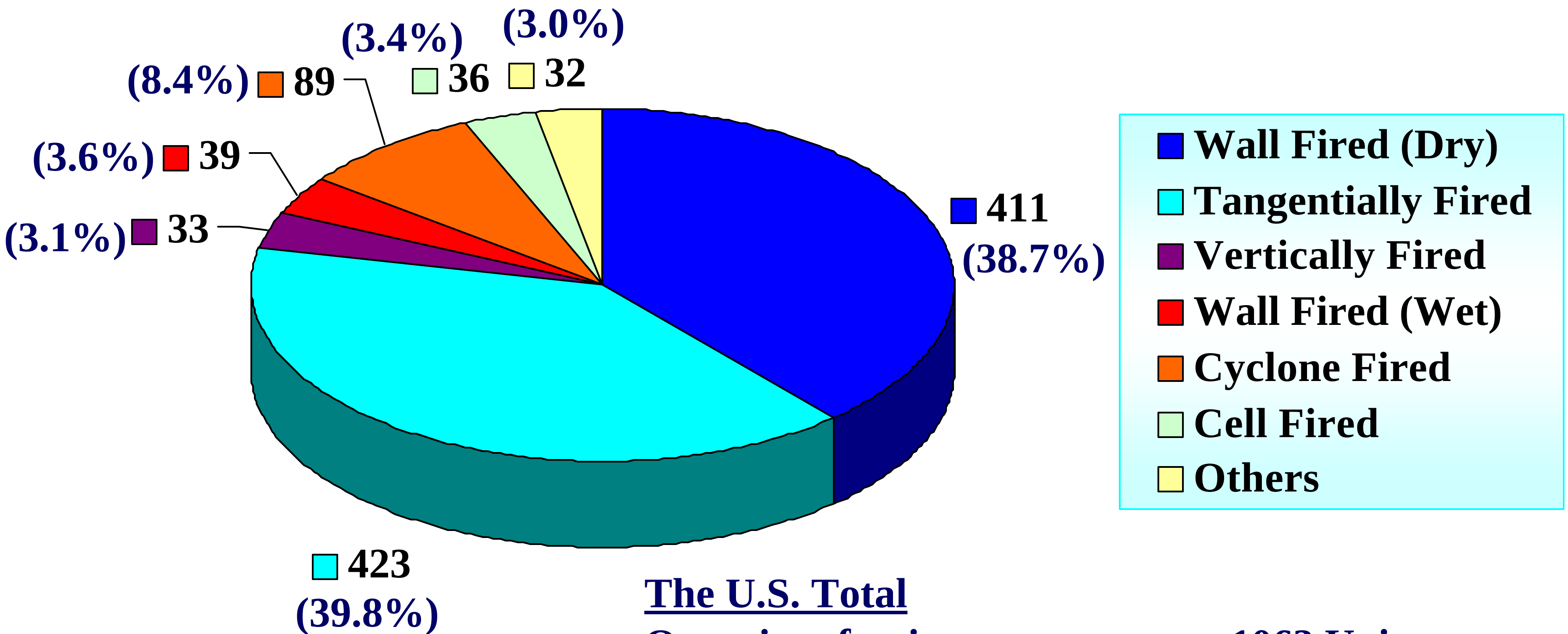
HITACHI ZOSEN ENGINEERING U.S.A. LTD.

Over View

SCR Catalyst Testing on USHS and PRB Coals

- **The U.S. Coal-fired Boilers (Boiler Types, Kind of Coal)**
- **Analysis of the Fly Ash Properties**
- **Influence on the SCR Catalyst for the U.S. Coal-fired Boiler application**
- **Testing**
  - **Catalyst Poisoning (Fly Ash, As_2O_3, Acid Gases)**
  - **Plugging**
  - **Erosion**
- **Operational Experiences**
  - **Catalyst Activity**
  - **SO_2 Oxidation**
  - **Plugging**
  - **Erosion**
- **Conclusion**

Summary of the U.S. Coal Fired Boilers

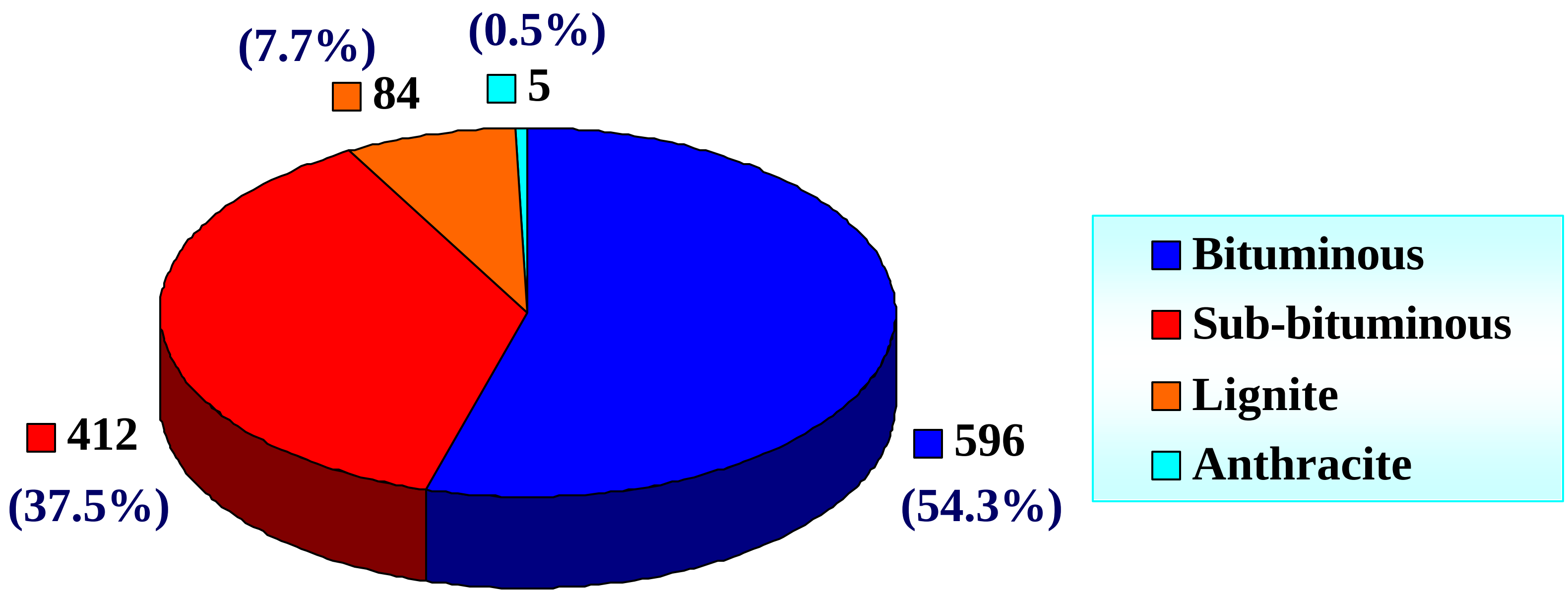


The U.S. Total

Quantity of units	**: 1063 Units**
Electric Generating Capacity	**: 327 GWe**
NOx Emission	**: 5,996,000 ton/year**

Source : DOE Fossil Energy – Low NOx Clean Technology Burners (1990)

Summary of the U.S. Coal Production

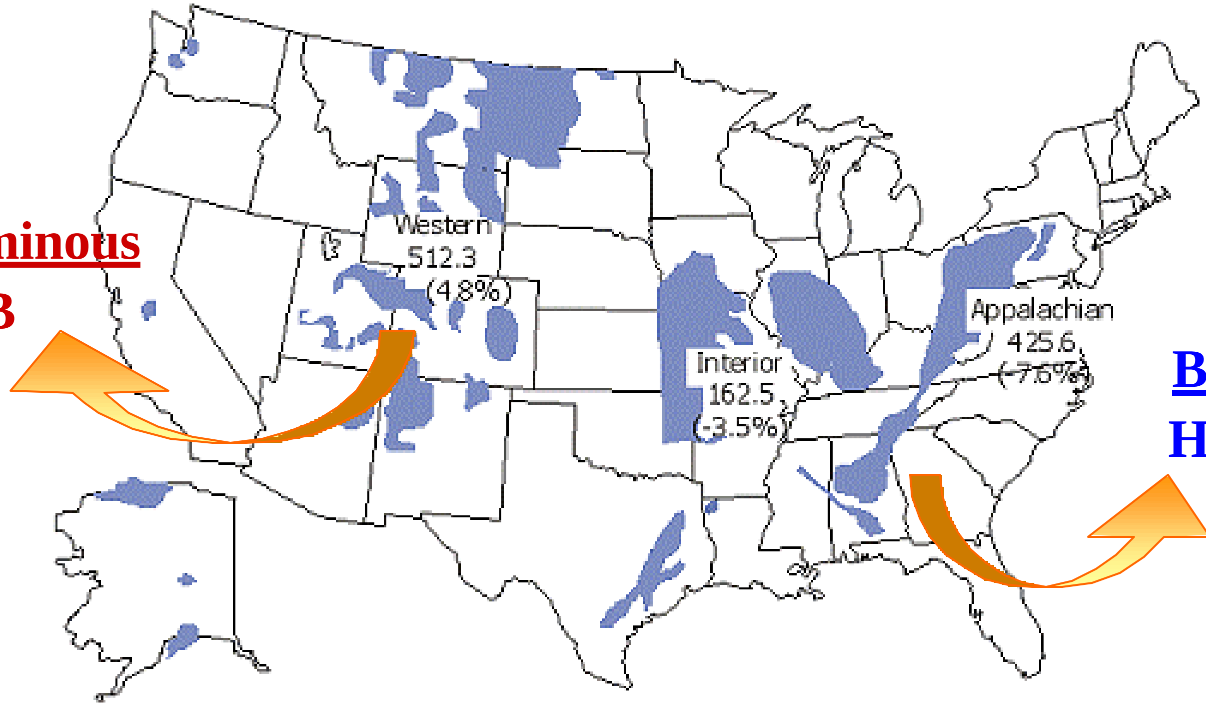


U.S. Total : 1,100 million short ton / year

Source : Coal Industry Annual 1999, DOE/EIA

The U.S. Coal Production

<u>Sub-bituminous</u>
PRB



<u>Bituminous</u>
High Sulfur

Source : Energy Information Administration

Coal Properties Analysis

	Bituminous (Japan)	USHS	PRB
As Received [wt%]			
Moisture	12.0	11.2	**27.0**
Ash	13.7	10.9	5.0
Moisture and ash-free [wt%]			
Carbon	80.5	80.8	76.2
Hydrogen	5.1	4.9	5.4
Nitrogen	1.6	1.6	1.1
Sulfur	0.9	**2.6**	0.4
Oxygen	11.9	10.1	16.9
HHV [Btu/lb]	11,640	11,260	**8,760**

USHS : the U.S. High Sulfur Bituminous Coal

Fly Ash Properties Analysis (1)

Boiler Type		Dry-bottom	Wet-bottom	
Fly Ash Re-Circulation		**No**	**No**	**Yes**
Coal		**USHS**	**USLS**	**USHS**
Na_2O	[wt%]	2.1	0.9	1.6
K_2O	[wt%]	2.5	3.0	2.8
MgO	[wt%]	1.9	2.5	.
CaO	[wt%]	3.8	6.6	4.1
Fe_2O_3	[wt%]	16.9	15.4	23.9
Al_2O_3	[wt%]	22.8	24.3	20.1
SiO_2	[wt%]	47.3	43.5	38.8
TiO_2	[wt%]	1.4	1.5	1.5
As	[ppm]	70	75	**320**
Fouling Index	[.]	0.38	0.41	0.54

Fly Ash Properties Analysis (2)

Boiler Type		**Dry-bottom**		
Fly Ash Re-Circulation		**No**	**No**	**No**
Coal		**Bituminous (Japan)**	**USHS**	**PRB**
Na_2O	[wt%]	0.3	2.1	3.8
K_2O	[wt%]	0.5	2.5	1.4
MgO	[wt%]	1.8	1.9	2.5
CaO	[wt%]	8.2	3.8	**28.3**
Fe_2O_3	[wt%]	6.1	16.9	7.0
Al_2O_3	[wt%]	31.4	22.8	17.8
SiO_2	[wt%]	48.4	47.3	33.1
TiO_2	[wt%]	1.3	1.4	1.8
As	[ppm]	6	70	12
Fouling Index	[-]	0.21	0.38	**0.82**

Influence on the SCR Catalyst for the U.S. Coal-fired Boiler Application

Items to be Considered			PRB	USHS	
			Dry	Dry	Wet-Re
Poisoning	**by Fly Ash**	Ca	**A**	B	B
		Na, K	B	B	B
	by As_2O_3		C	B	**A**
	by Acid Gas		C	B	B
Erosion by Fly Ash			B	B	B
Cell Plugging by Fly Ash			**A**	B	B

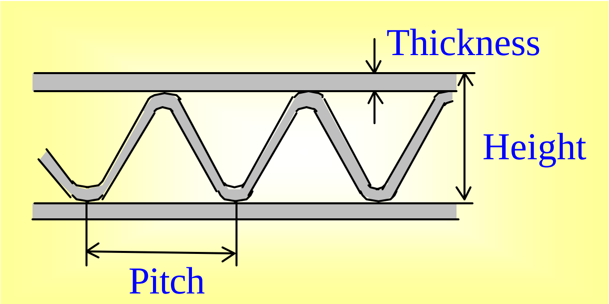
Wet-Re : Wet Bottom Boiler with Fly Ash Re-circulation Application

- **Degree of Consideration** : A (High) . . B (Middle) . . C (Low)

Catalyst Testing for the U.S. Coal-fired Boiler Application

- Poisonings
  - by Fly Ash
  - by Gaseous Arsenic (As_2O_3)
  - by Acid Gases (SO_3,HCl, CH_4, CO)
- Erosion by Fly Ash
- Cell Plugging by Fly Ash

Catalyst Specification of NOXNON700



- **Shape : Corrugated Ceramic Honeycomb**
- **Substrate : Ceramic Fiber Matrix (CFM)**
- **Active Metal : TiO_2 - V - W**

Catalyst Type			**S-3D**	**S-6**
Cell Dimension	**Pitch**	[mm]	11.0	15.8
	Height	[mm]	6.7	9.8
	Thickness	[mm]	0.8	1.0
Contact Surface Area		[m^2/m^3]	600	450
Open Space Area		[%]	76	70
Weight		[kg/m^3]	770	730

Definition of Catalyst Activity

Assume that the Reaction is First Order with respect to NOx or NH_3.

$$K = - Av \ \ln (1 - x / r)$$

K = Catalyst Activity

Av = Area Velocity

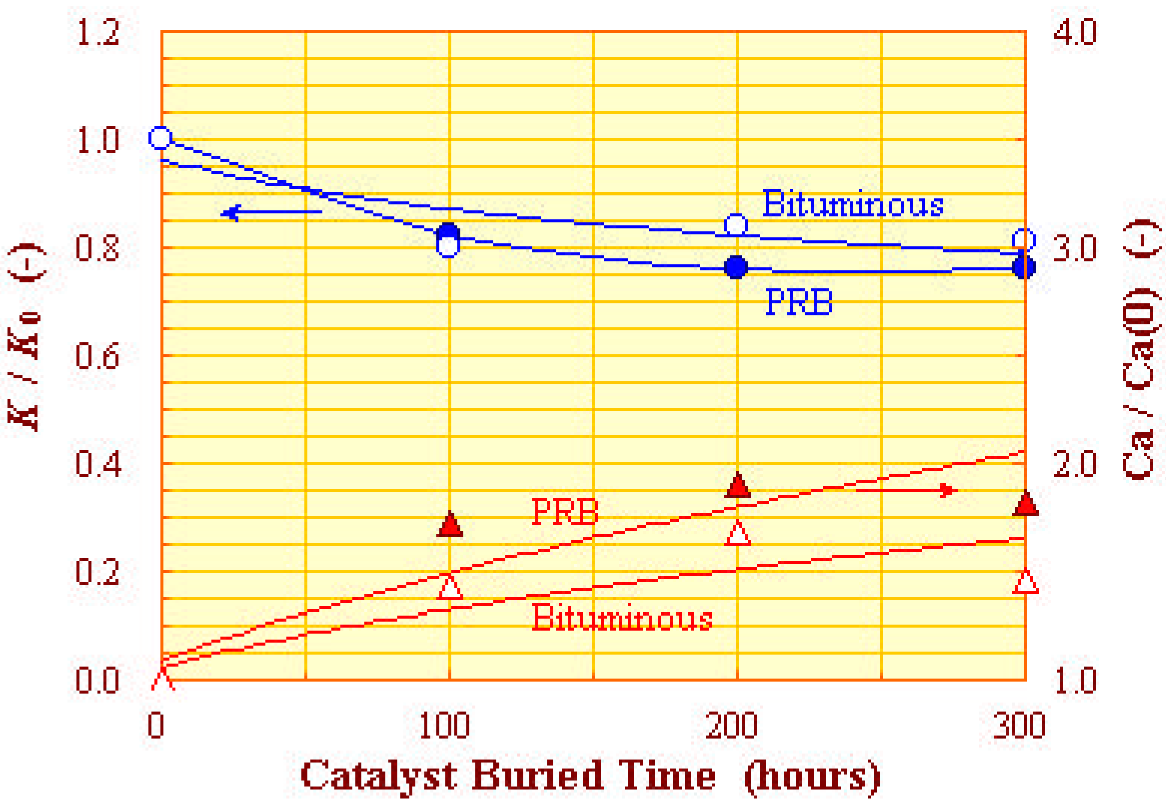
x = NOx Removal Efficiency

r = Inlet NH3 / NOx molar ratio

Then… K / K_0 Represents for the Degree of Catalyst Deactivation.

Poisoning by Fly Ash (1)

Simulation of Steady State



AV : 5.8 SCFM/ft^2, NH_3 / NOx : 1.0
(100 Nm/h)

Experiment (Temp: 660 F)

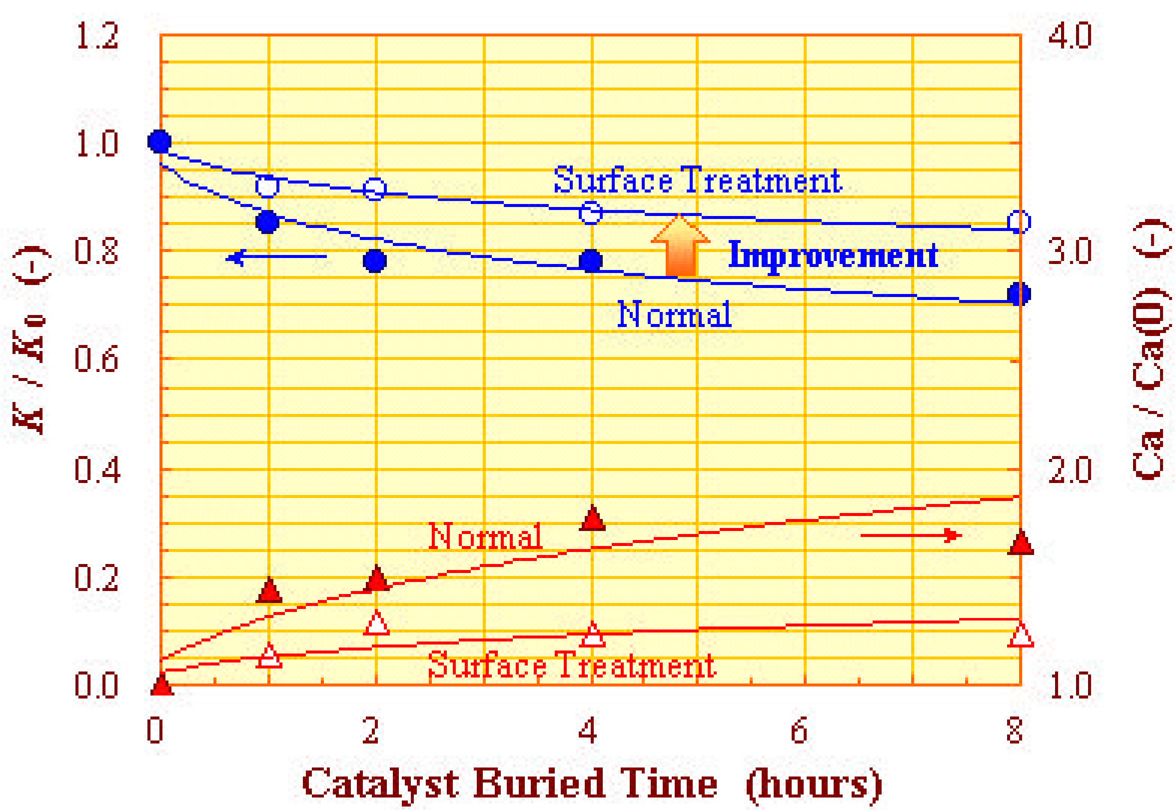
- Accelerated Catalyst Test ;
  By Buried to the Fly Ash

Activity (Temp: 660 F)

- Deactivation ;
  Main cause by
  Accumulation of Calcium
- Deactivation Rate of PRB ;
  Slightly Higher than
  Bituminous Coal

Poisoning by Fly Ash (2)

Simulation during Start-up & Long Term Shut down (PRB Coal)



AV : 5.8 SCFM/ft^2, NH_3 / NOx : 1.0
(100 Nm/h)

Experiment (AMB, RH 100%)

- Accelerated Catalyst Test ;
  By Buried to the Fly Ash

Activity (Temp: 660 F)

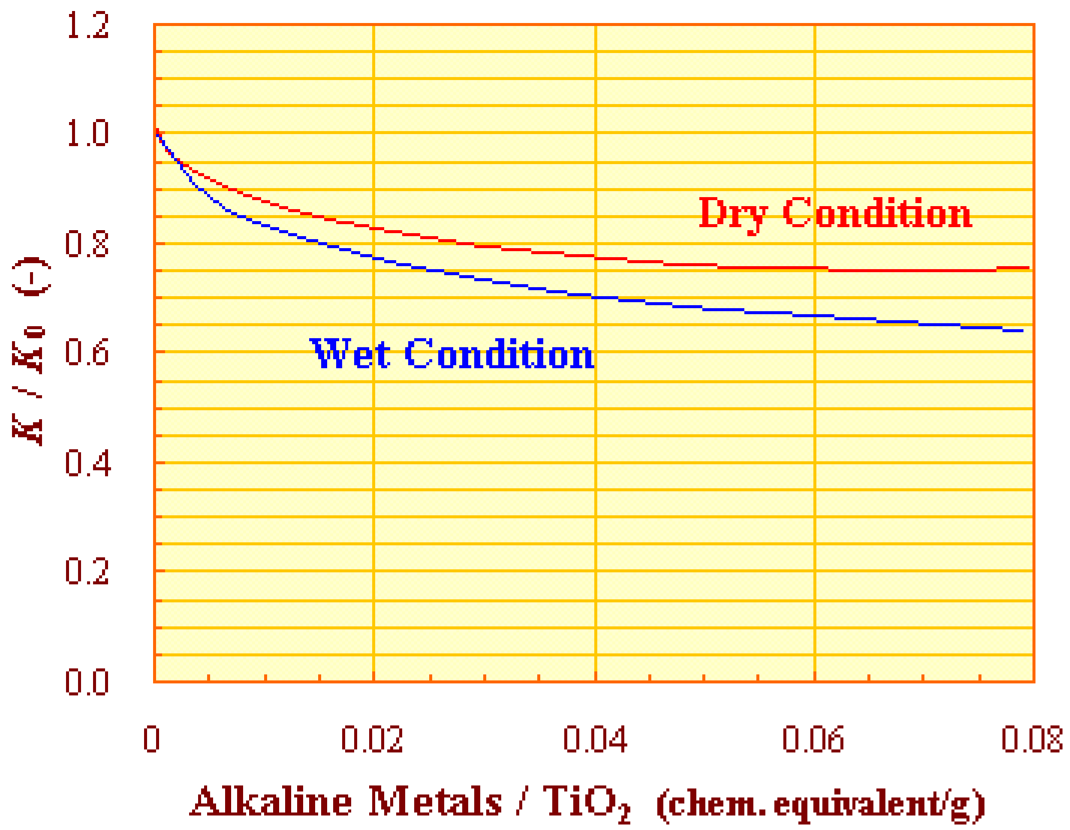
- Deactivation ;
  About 50 Times faster than Steady State

Countermeasure

- Surface Treatment ;
  Effective to the Poisoning by Calcium

Poisoning by Fly Ash (3) - Summary

Accelerated Catalyst Test – By Buried to the Fly Ash



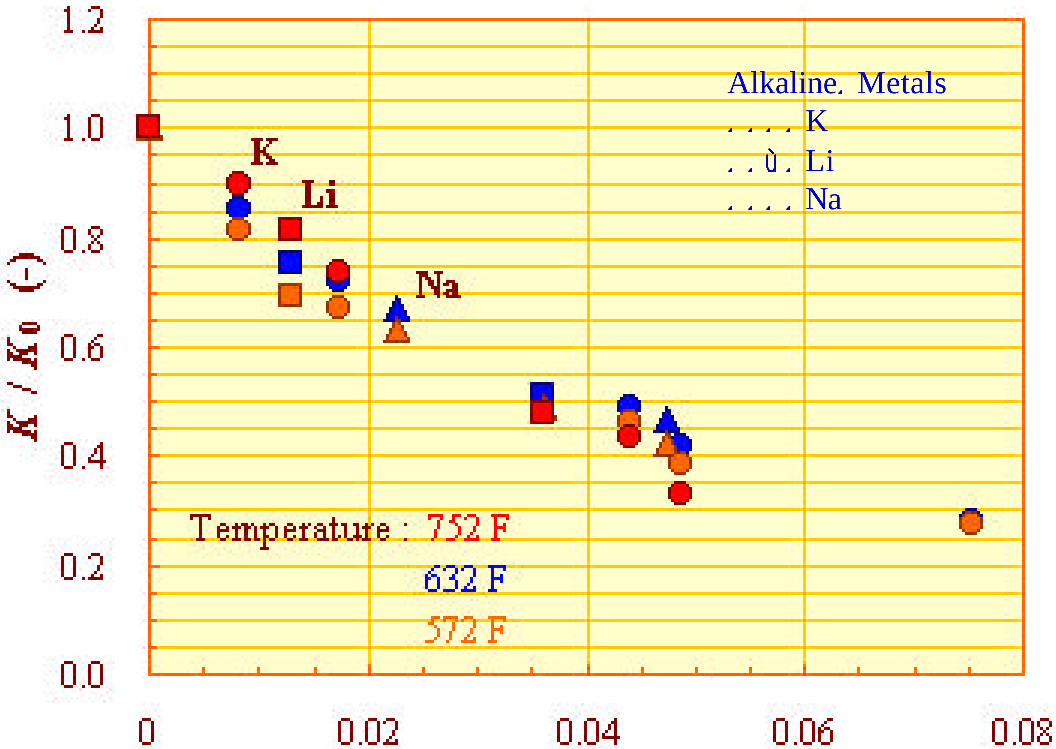
Activity (Temp. : 660 F)

- Deactivation ;

  Different between Dry and Wet Conditions

Poisoning by Alkaline Metals

Simulation of Wet Condition



AV : 2.5 SCFM/ft^2, NH_3 / NOx : 1.2
(43 Nm/h)

Experiment (AMB)

- Accelerated Catalyst Test ;
  By Impregnated to the K^+, Na^+, Li^+ Solution

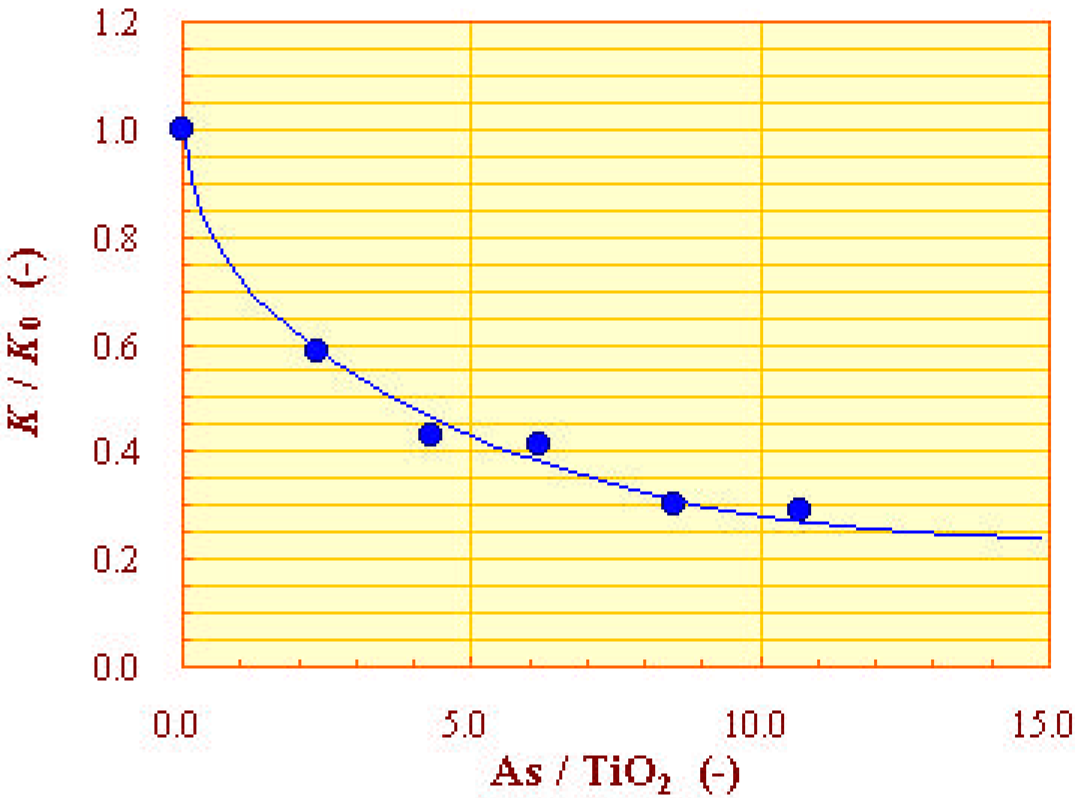
Activity (Temp. in the Figure)

- Deactivation ;
  High by Accumulation of K^+, Na^+, Li^+ , but No Difference in the Metals

  Slightly Dependence with SCR Reaction Temperature

Poisoning by Gaseous Arsenic (1)

Simulation of Wet-bottom boiler with Fly Ash Re-circulation



AV : 5.8 SCFM/ft^2, NH_3 / NOx : 1.0
(100 Nm/h)

Experiment (Temp: 660 F)

- Accelerated Catalyst Test ;
  By Exposed to the Flue Gas with 15-20 ppm of As_2O_3

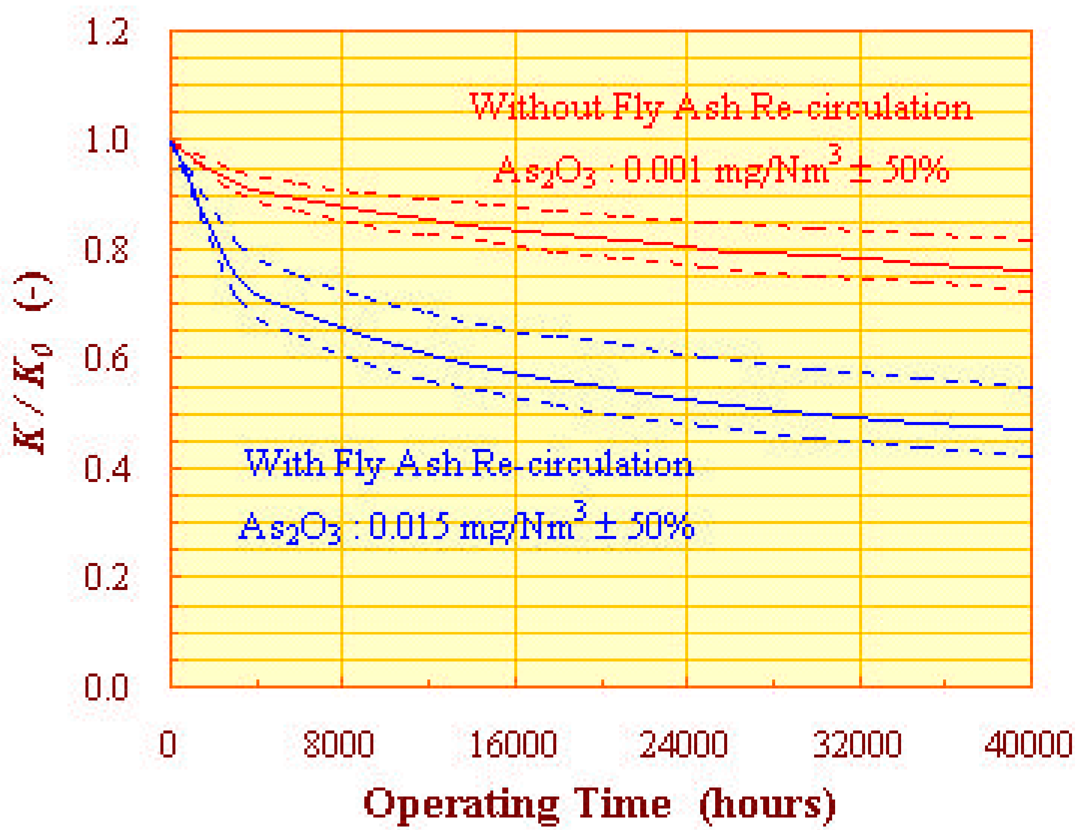
Activity (Temp: 660 F)

- Deactivation ;
  High by Deposition of As_2O_3

  20% of Initial Activity Remained with As Saturated layer

Poisoning by Gaseous Arsenic (2)

Comparison about Fly Ash Re-circulation



AV : 5.8 SCFM/ft^2, NH_3 / NOx : 1.0
(100 Nm/h)

Calculation (Temp: 660 F)

- No Fly Ash Re-circulation ;
  As_2O_3 : 6. 10^{-8} lb/SCFM (0.001 mg/Nm^3)
- Fly Ash Re-circulation ;
  As_2O_3 : 15 times higher (0.015 mg/Nm^3)

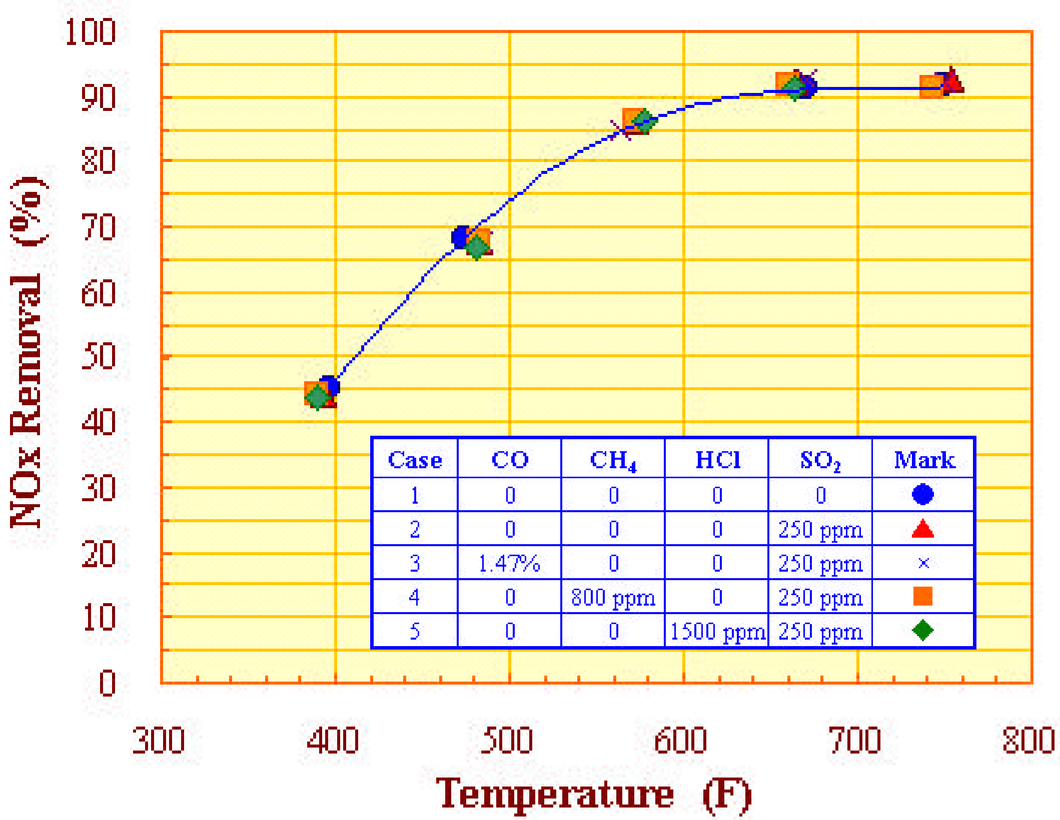
Activity

- Deactivation Rate in Fly Ash Re-circulation ;

  Much Higher than in No Fly Ash Re-circulation

Poisoning by Acid Gases (1)

Simulation of Steady State (Initial Activity)



Case	CO	CH_4	HCl	SO_2	Mark
1	0	0	0	0	●
2	0	0	0	250 ppm	▲
3	1.47%	0	0	250 ppm	×
4	0	800 ppm	0	250 ppm	■
5	0	0	1500 ppm	250 ppm	◆

AV : 2.5 SCFM/ft^2, NH_3 / NOx : 1.2
(43 Nm/h)

Experiment (Temp. in the Figure)

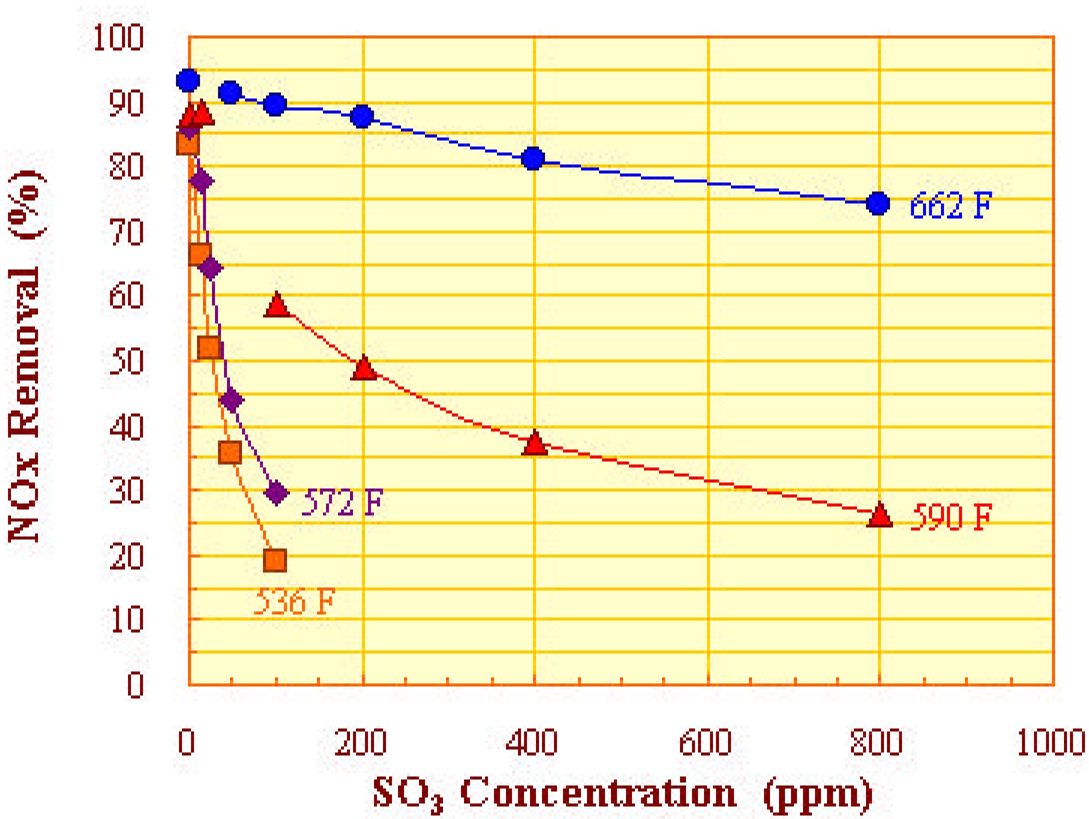
- Normal Catalyst Test ;
  By Exposed to the Flue Gas with HCl, SO_2, CH_4, CO

Activity

- Deactivation ;
  None with 1,500 ppm of HCl
  250 ppm of SO_2
  800 ppm of CH_4
  1.47 % of CO

Poisoning by Acid Gases (2)

Simulation of Steady State (Initial Activity)



AV : 4.35 SCFM/ft^2, NH_3 / NOx : 2.0
(75 Nm/h)

Experiment (Temp. in the Figure)

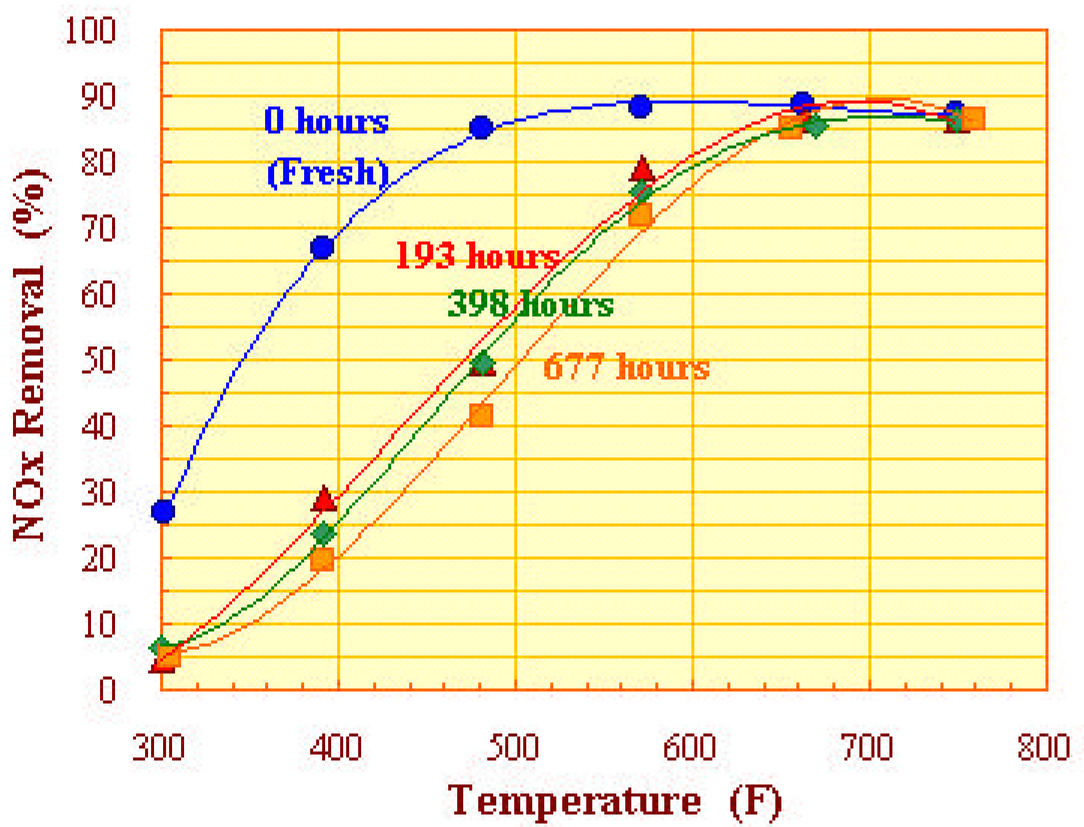
- Normal Catalyst Test ;
  By Exposed to the Flue Gas with SO_3

Activity

- Deactivation Rate ;
  Proportion to SO_3 Concentration, but Slightly Dependence at 660 F

Poisoning by Acid Gases (3)

Simulation of Steady State (Long-term Activity)



AV : 2.5 SCFM/ft^2, NH_3 / NOx : 1.5
(43 Nm/h)

Experiment (Temp: 680 F)

- Accelerated Catalyst Test ;
  By Exposed to the Flue Gas with 1,000 ppm of SO_3 during 193, 398, 677 hours

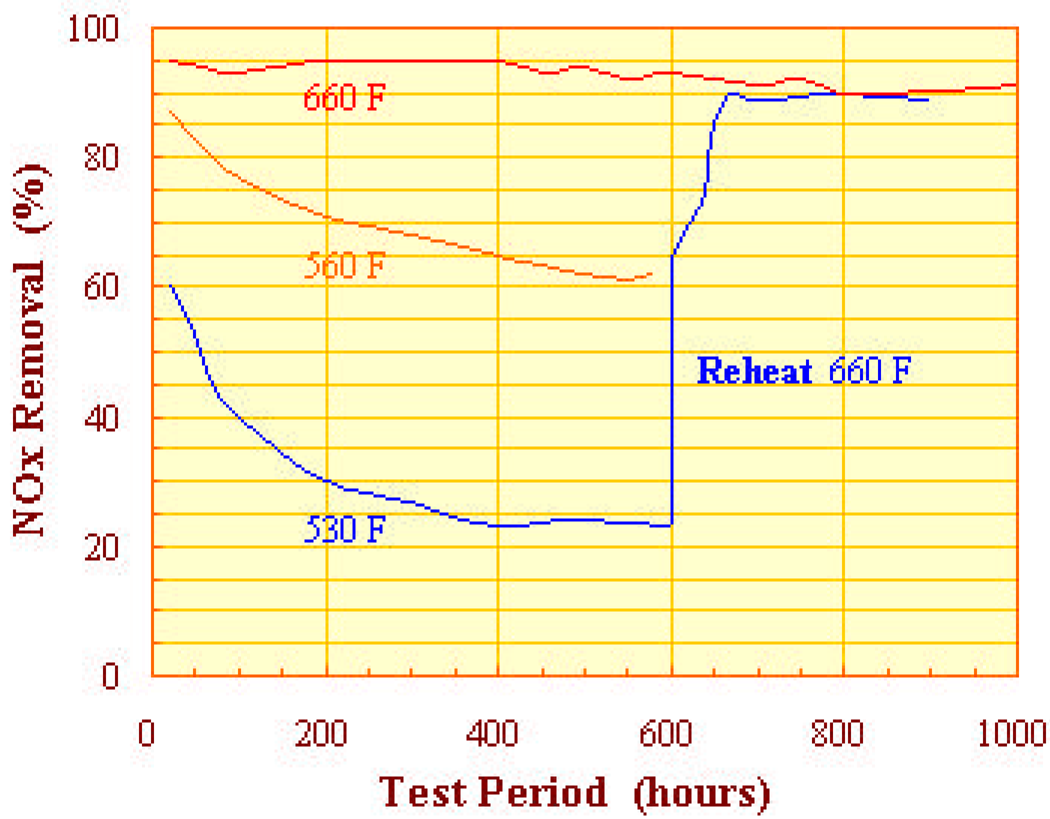
Activity (Temp. in the Figure)

- Deactivation Rate ;
  Proportion to Exposing Time, but None over 650 F

  High below 600 F

Poisoning by Acid Gases (4)

Simulation of Catalyst Revival



AV : 0.9 SCFM/ft^2, NH_3 / NOx : 1.0
(15.5 Nm/h)

Experiment (Temp. in the Figure)

- Normal Catalyst Test ;
  By Exposed to the Flue Gas with 22 ppm of SO_3

Activity

- Re-activation ;
  Enable to Revival for the SO_3 Poisoning by heat-up over 660 F

Cell Plugging (1)

EXPERIMENTAL APPARATUS

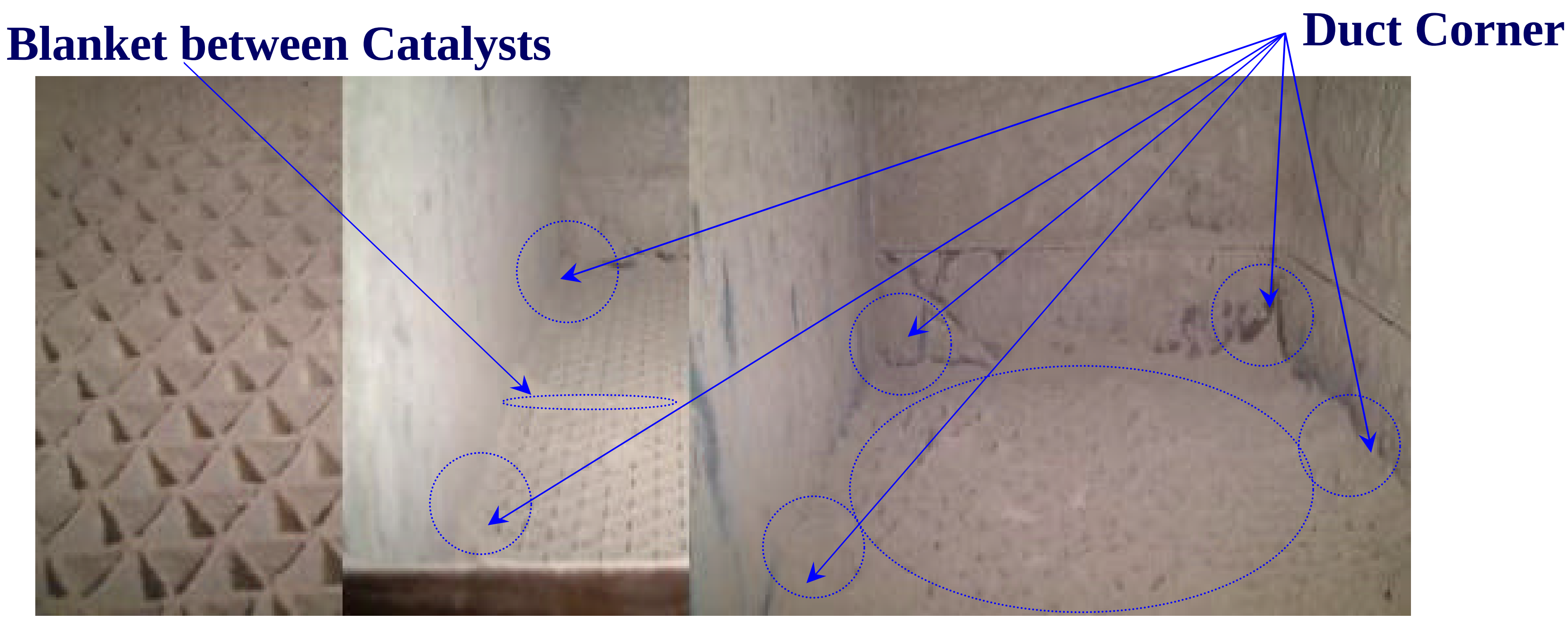
T

<u>Test Conditions</u>

- S-3D Catalyst
- Fly Ash from PRB Coal
- 240 grains/SCF
- 716 F
- 3.3 – 16.5 ft/s

Cell Plugging (2)

Simulation of Steady State (PRB Coal)



16.5 ft/s (5 m/s)
96 hours

9.9 ft/s (3 m/s)
65 hours

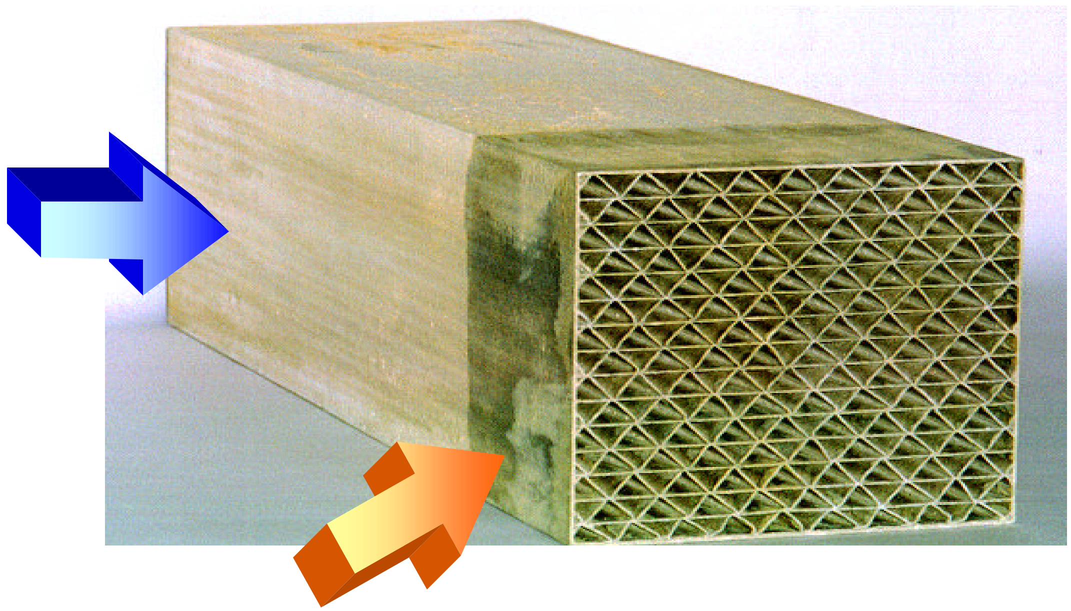
3.3 ft/s (1 m/s)
2 hours

Design Base 10 Std.ft/s (at 660 F) = 21.6 ft/s

Erosion by Fly Ash (1)

Improvement Catalyst

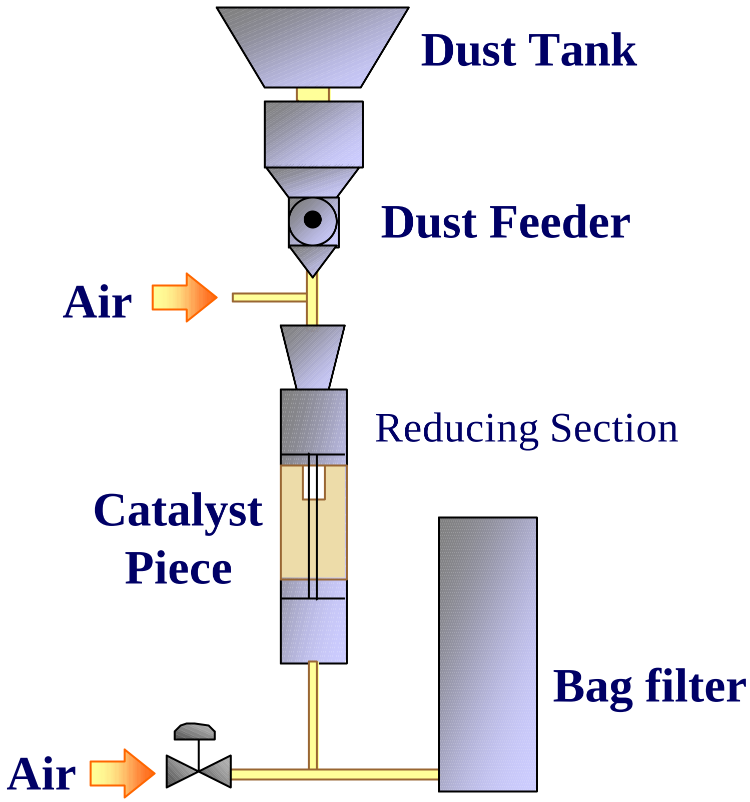
Surface Coating

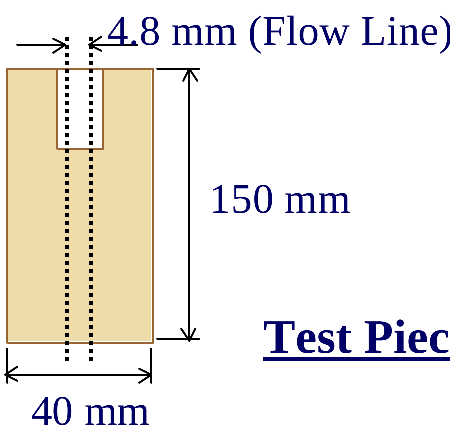


Edge Coating

Erosion by Fly Ash (2)

EXPERIMENTAL APPARATUS





Test Piece

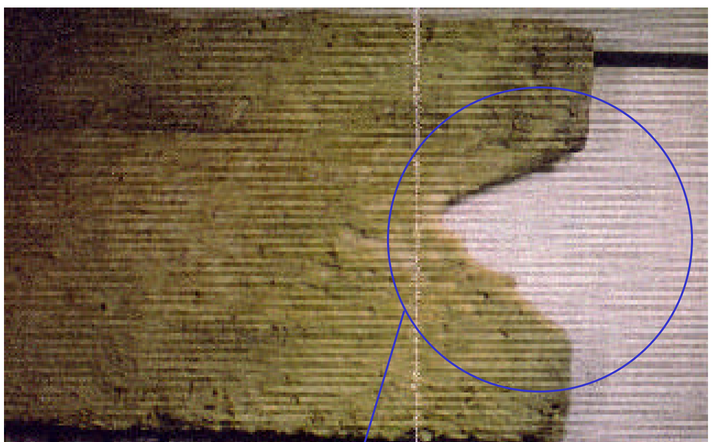
Test Conditions

- Fly Ash from Bituminous Coal
- 100 μm (Average Diameter)
- 11,200 grains/SCF
- 55 ft/s (16.5 m/s)

Erosion by Fly Ash (3)

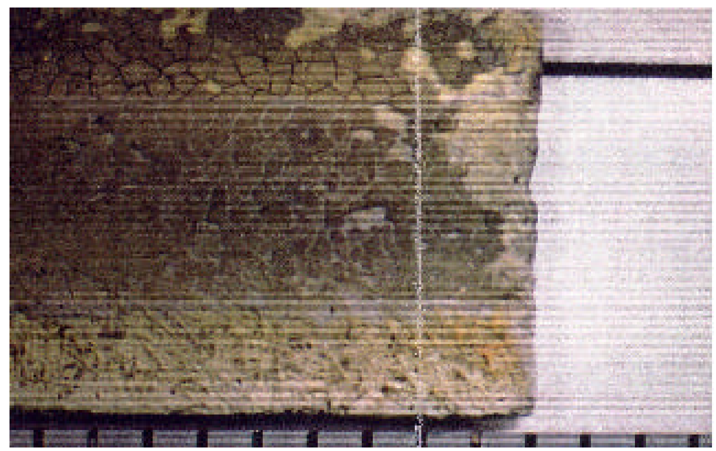
Simulation of Steady State

Without Edge Coating



Edge Erosion

With Edge Coating



Accelerated Test equal to 15,000 hours Operation

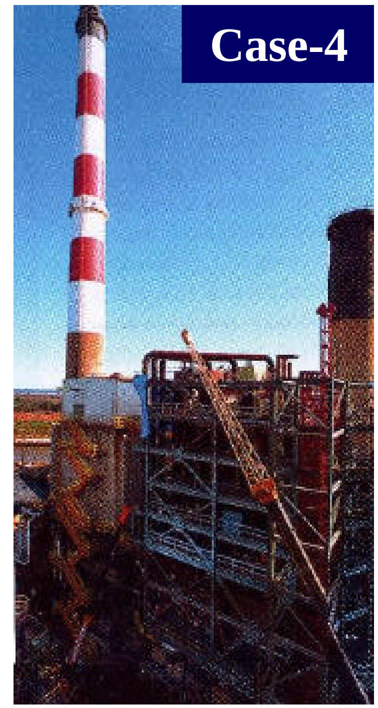
Operational Experiences for Coal-fired Boilers (1)

SCR Plant	Purpose	Remarks	Status
Case-1 (Japan)	Replacement	Typical Case for High Dust Application Dust Loading : 240 grains/SCF	Continued
Case-2 (Japan)	Demonstration	Typical Case for High SOx Application SOx Concentration : 2,120 ppm	Continued
Case-3 (Japan)	Pilot Test	Typical Case for High Efficiency Application NOx Removal Efficiency : 80 %	Finished
Case-4 (the U.S.)	Pilot Test	"SCR Demonstration Program" Clean Coal Technology promoted by the DOE	Finished

Operational Experiences for Coal-fired Boilers. (2)

Location : Shimonoseki, Japan
Load : 175 MW
Type : Dry Bottom
Coal : Bituminous (Sulfur 0.8%)

Location : Isogo, Japan
Load : 265 MW
Type : Dry Bottom
Coal : Bituminous

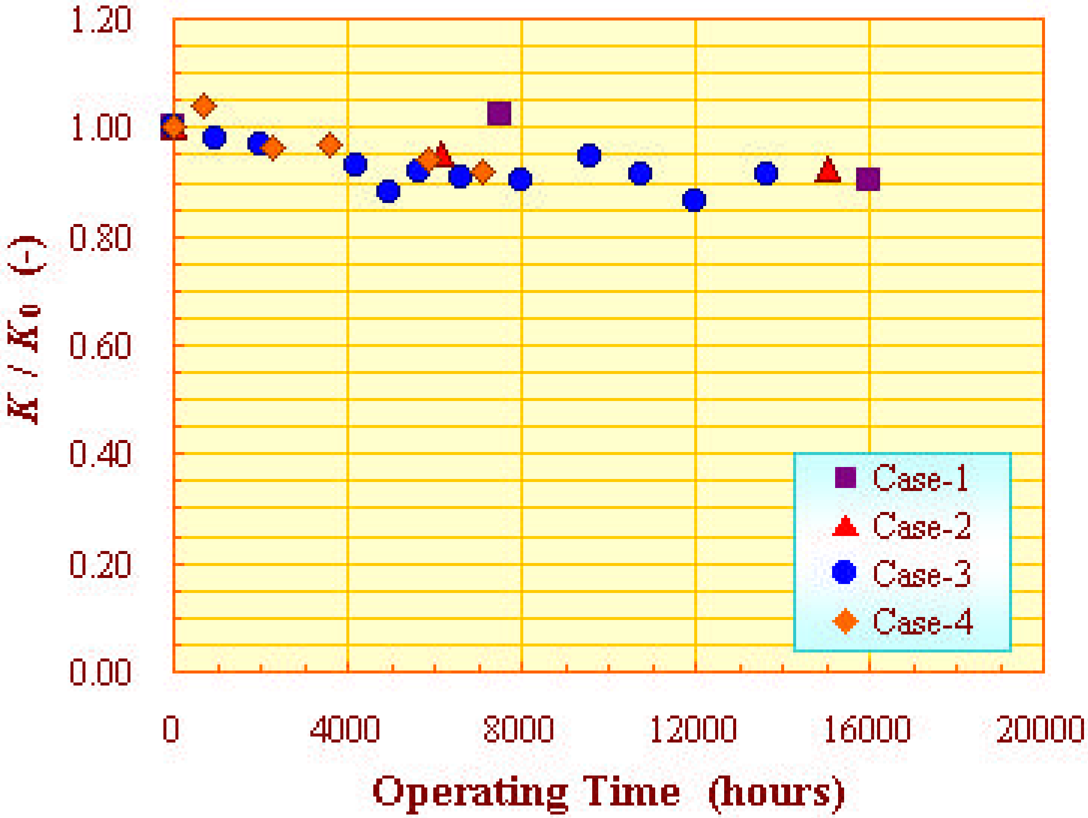


Location : Pensacola, Florida
Load : 75 MW
Type : Dry Bottom
Coal : IllinoisNo.6 (Sulfur 2.3%)

Operational Experiences for Coal-fired Boilers. (3)

		Case-1	Case-2	Case-3	Case-4
Boiler Type		Dry-bottom	Dry-bottom	Dry-bottom	Dry-bottom
Coal		Bituminous	Bituminous	Bituminous	Bituminous
Flue Gas Flow Rate	[SCFM]	342,000	549,000	930	420
SCR Temperature	[F]	698	734	662	700
Dust Loading	[gr/SCF]	240	160	320	160
SOx	[ppm]	1,600	2,120	450	2,000
Inlet NOx	[ppm]	570	340	180	400
NOx Removal Efficiency	[%]	50	66	80	80
Leak Ammonia	[ppm]	< 5	< 10	< 5	< 5

Catalyst Activity



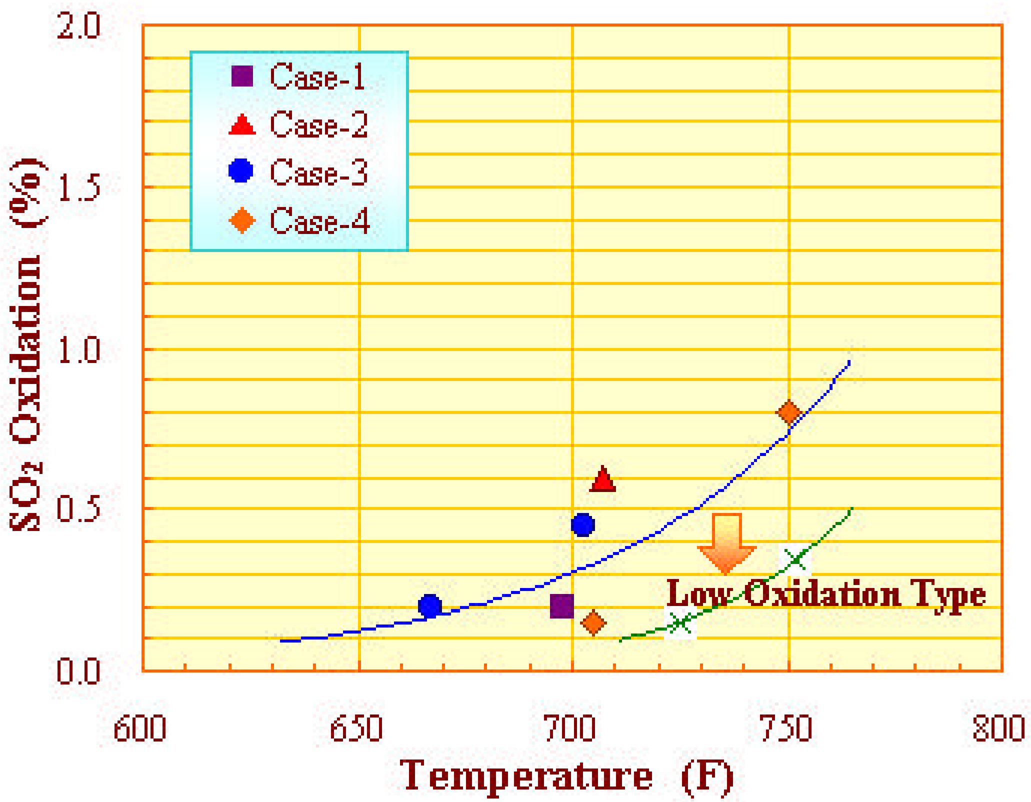
Catalyst Activity

- Deactivation Rate ;

  No Difference in the 4 cases

  Over 80% of Initial Activity Remained at 2 years Operation

SO_2 Oxidation



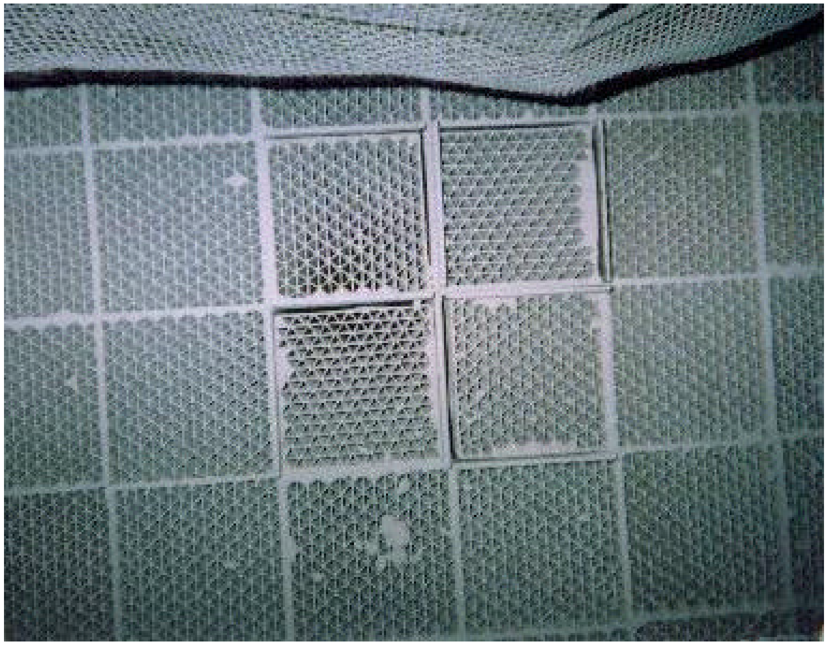
SO_2 Oxidation

- SO_2 Oxidation Rate ;
  Less than 1.0 % at 750 F
- Low SO_2 Oxidation Type ;
  Reducing 50 % of SO_2 Oxidation Rate Moreover

Cell Plugging (1)

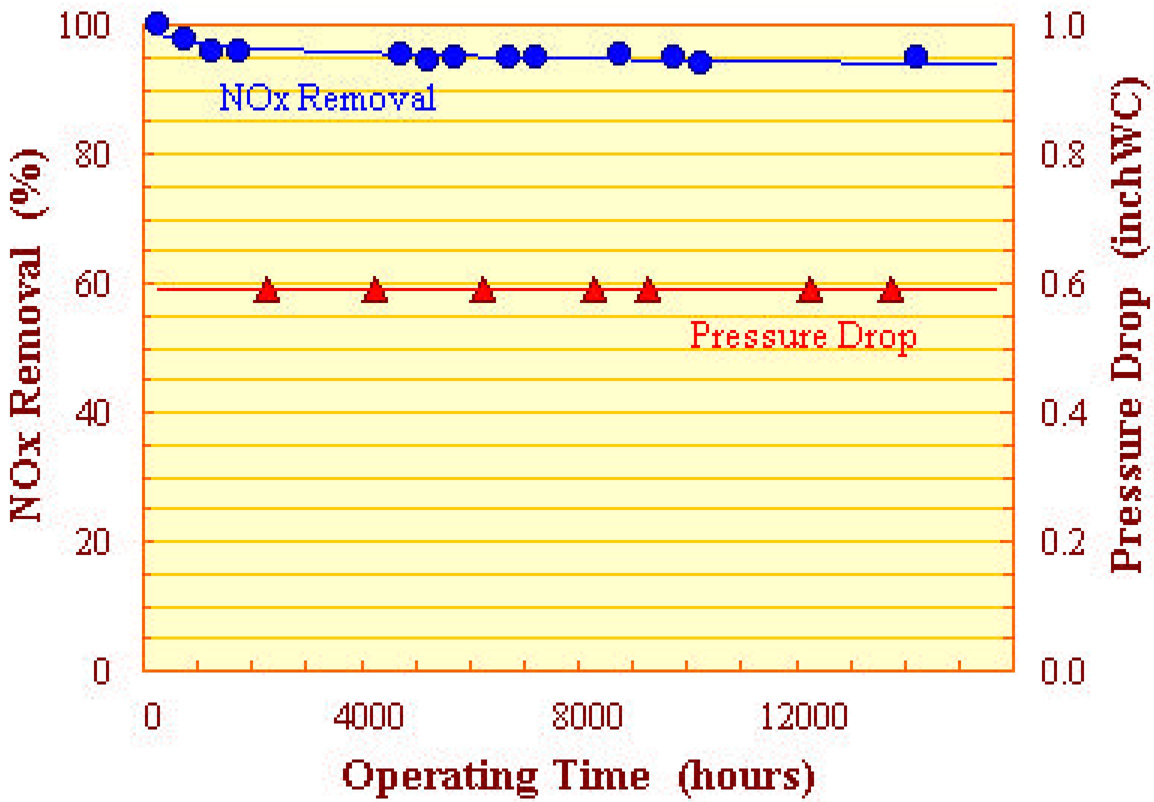
Case-1

Case-2



- **No dust accumulation has been found during 2 years operation.**

Cell Plugging (2)



Case-3

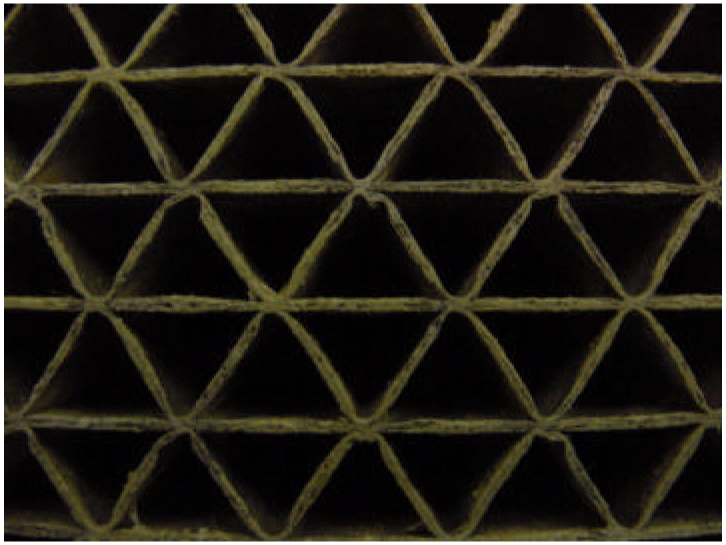
Cell Plugging

- Pressure Drop ;

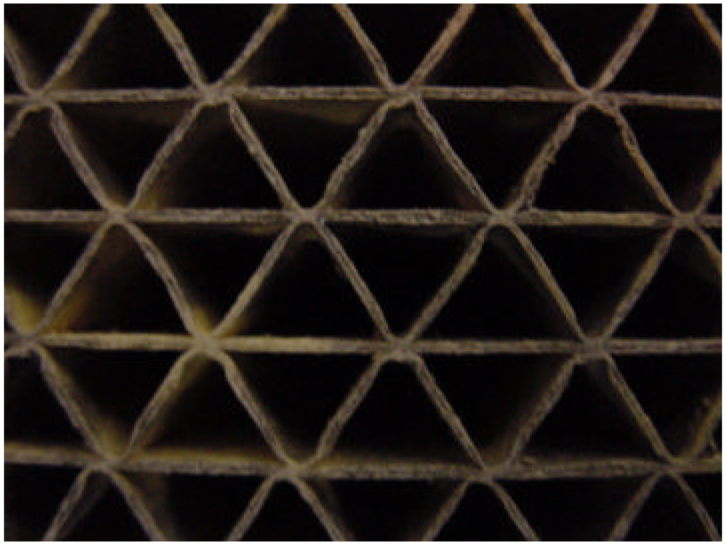
  Stable During 2 Years Operation

Erosion (1)

Fresh Catalyst



Exposed Catalyst

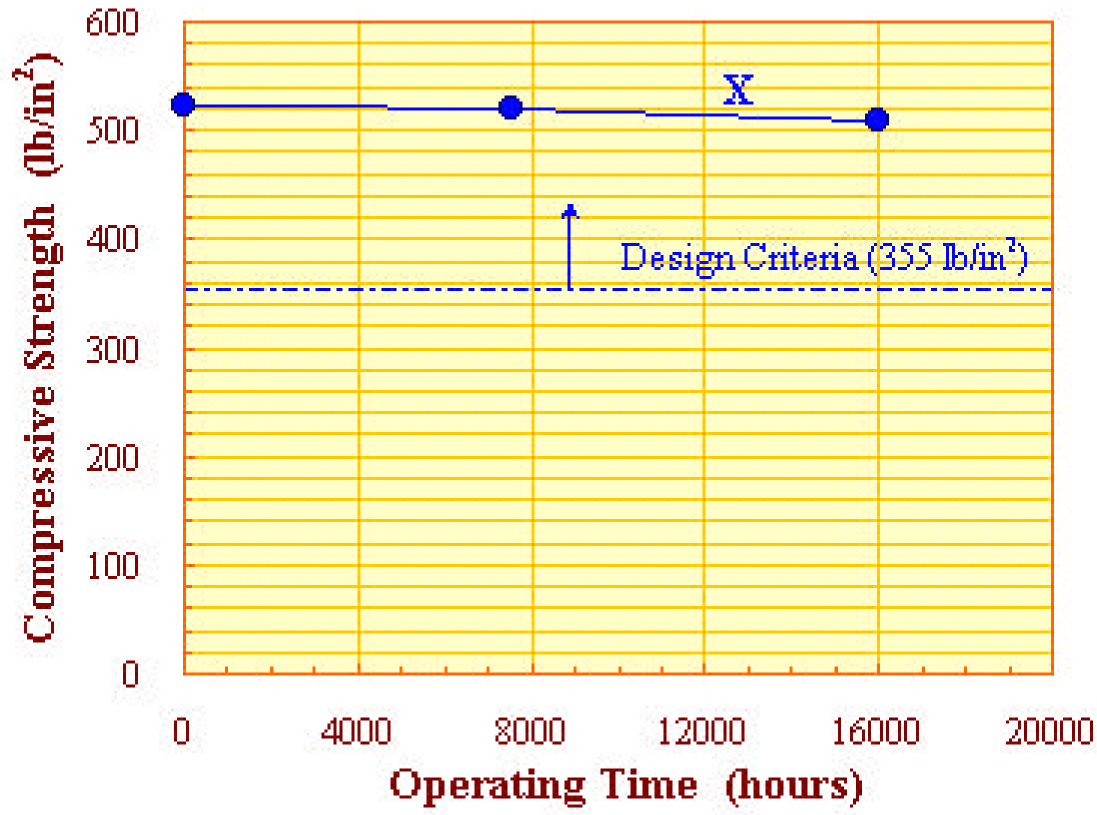


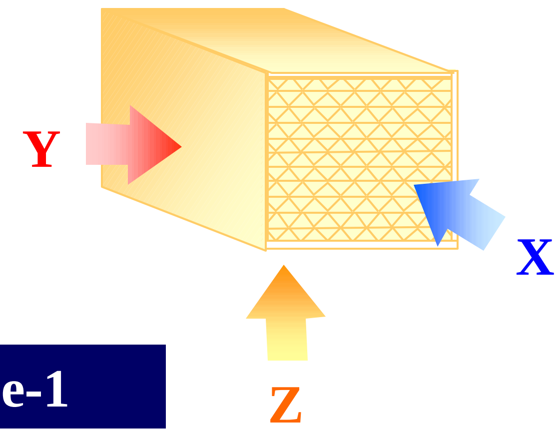
- **No erosion has been found during 2 years operation.**

Case-1

Dust Loading : 240 grains/SCF
Exposed Period : 2 years

Erosion (2)





Case-1

Erosion

- Compressive Strength ;
  Stable During 2 Years Operation

Design Criteria of Products

X : 355 lb/in^2
Y : 101 lb/in^2
Z : 43 lb/in^2 (S-6 Type)

Pilot Test for PRB at A Power Station (1)

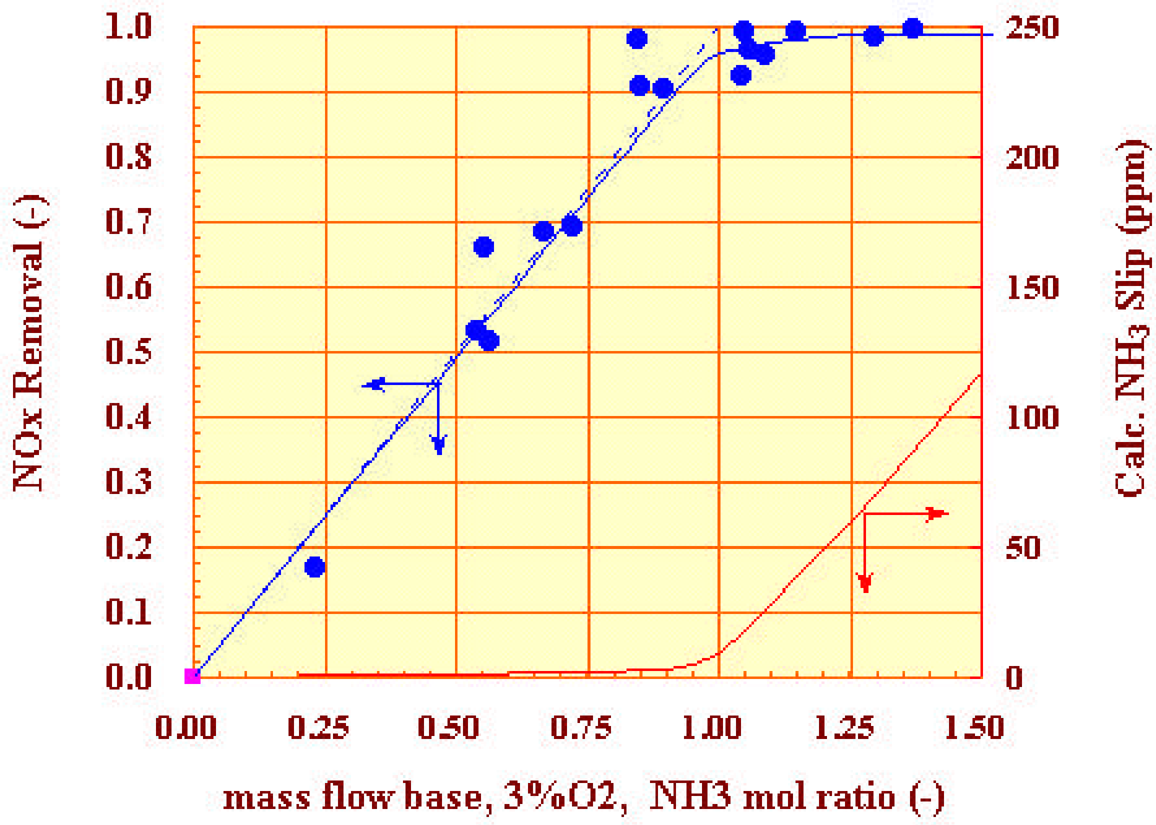
Application to PRB Coal

Test Conditions		
Flue Gas Flow Rate	[SCFM]	60
SCR Temperature	[F]	610
Dust Loading	[gr/SCF]	.
SOx	[ppm]	500
Inlet NOx	[ppm]	230
NOx Removal Efficiency	[%]	> 80
Leak Ammonia	[ppm]	< 5

Location : North America
Load : 500 MW
Type : Dry Bottom

Pilot Test for PRB at A Power Station (2)

Catalyst Performance



Conclusion

- **High Sulfur Bituminous Coal for Dry-bottom Boilers**
  - Similar countermeasures as the Japanese experiences.
- **PRB Coal for Dry-bottom Boilers**

  In addition to the same consideration as the Japanese experiences ;
  - Countermeasure to minimize the catalyst deactivation by calcium in the fly ash
  - Necessity of the soot blowing device to avoid the fly ash accumulation
- **Any Kind of Coal for Wet-bottom Boilers with the Fly Ash Re-circulation**
  - Examination of As2O3 in the flue gas to clarify the catalyst deactivation rate
  - Life management plan suitable for the operation conditions required
- **Common**
  - Preservation of the catalyst to avoid the dewing on the catalyst surface

    with fly ash during a long-term shut down period.